Quantitative Analysis of WC Grain Shape in Sintered WC-Co Cemented Carbides

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The morphology of WC grains is examined by *ab initio* calculations, and by transmission electron microscopy in a WC-Co cemented carbide. Two compositions are studied to determine the effect of carbon chemical potential on the shape development. The WC grains are found to be truncated triangles, and the grain morphology is adequately reproduced by the *ab initio* calculations. The energy difference between the two types of grain facets is shown to be due to the formation of stronger bonds with more covalent character between low coordinated W and Co atoms at one type of facet.

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Materials such as metals and ceramics are nearly always composed of crystallite grains. The shape and size of the grains to a large degree govern the macroscopic properties of the material, so they are of vital importance both from a scientific point of view as well as from a technological standpoint [1,2]. The predictive power of ab initio calculations combined with quantitative experimental investigations provides a promising approach in elucidating the physical character of grain morphology, but the very large gap between the *ab initio* domain and the scale of real grains makes such an approach a real challenge. However, with a judicious choice of appropriate modeling techniques, ab initio calculations may provide important insight. In particular, this is true in situations with materials characterized by many mixed types of interactions, such as metal-ceramic systems [3].

One important example is WC-Co cemented carbides [4], which are paid much attention due to their high hardness, ductility, and wear resistance making them excellent tool materials in a wide range of applications including, e.g., cutting and milling. They are produced by liquid phase sintering of compacted mixtures of WC and Co powders where the C/W ratio is an important parameter which effects the size and morphological distributions of the carbide grains [5–8]. WC grains are often found in the form of truncated triangular prisms. The reason for this has been recognized to be due to the hexagonal geometry of WC, for which there are two types of prismatic (WC{1010}) surfaces which may give rise to an anisotropy in Co/WC interface energy [6,8].

In the present work, a quantitative analysis of the WC grain shape and its dependence on the carbon potential is performed. Using *ab initio* calculations, the interface energy of the different types of Co/WC{ $10\overline{10}$ } interfaces are assessed [9–13]. The relative energies of the two types of Co/WC{ $10\overline{10}$ } interfaces are used to determine the degree of faceting of the carbide grains. A quantitative experimental evaluation of the WC grains is also performed using transmission electron microscopy (TEM), by growing WC

crystals in controlled conditions and measure the shape and size of their basal plane. The difference between the two prismatic surfaces is revealed through an analysis of the electron structure.

Two compositions were selected to fix the C chemical potential to the C-rich (graphite) and W-rich (η) limits of the 2-phase field {WC + Co base binder} [14]. The C-rich alloy is located in the 3-phase field {WC + liquid + C(graphite)} while the W-rich alloy consists of the mixture {WC + liquid + (W, Co)₆C(η)} at the liquid phase sintering temperature (1450 °C). The Co content (24 wt %) was chosen sufficiently high to limit the contacts between WC grains but small enough to permit the thin foil preparation for TEM observations. The samples were prepared from powders of WC with 0.85 μ m as initial medium size. The compacted powders were sintered at 1450 °C for 10 h using a sintering furnace and a gas atmosphere enabling to control the C potential along the treatment, as previously described [6].

The microstructures of the heat-treated materials were observed by TEM using a JEM-3010. The foils for TEM were prepared by standard ion thinning beam method. Grains with sharp corners are sometimes found in the Crich alloy [Fig. 1(a)] but not in the W-rich [Fig. 1(b)]. Steps



FIG. 1. TEM images of WC grains viewed along $\langle 0001 \rangle$ showing the truncated triangular shape, where the anisotropy is larger in (a) the C-rich (graphite limit) alloys than in (b) the W-rich (η limit) alloys.

are not detected at the prismatic interfaces and the interfaces are always planar for the long facets and either planar or somewhat rounded for the short facets [15]. To quantify the shape, the parameter $r = \sum a_{\text{short}} / \sum a_{\text{long}}$, defined as the ratio of the sum of short side lengths to the sum of long side lengths of the basal plane polygon, was measured. If the basal plane is a regular hexagon, r reaches 1, if it is a triangle, r is equal to 0. Two sets of values, corresponding to the C-rich and W-rich alloys are observed. In each set, the r values are highly dispersed for grains smaller than a limit size a_1 , and more constant for larger grains. The rather constant r value measured for large grains, $a > a_1$, is considered to represent the equilibrium shape. The length *a* is taken to be the side length in the corresponding equilateral triangle. In the C-rich alloy, the r values range between 0.08 and 0.2 (0.14 ± 0.06) for $a > a_1 =$ 4.5 μ m. In the W-rich material, the r values are found to be (0.23 ± 0.03) for $a > a_1 = 2 \ \mu$ m. In each sample, the morphology of 25 grains was measured.

The equilibrium shape of WC grains is determined by the relative free interface energies, γ , of the grain facets. Since we experimentally find that the grains are bounded by interfaces formed from prismatic WC{1010} surfaces only, we restrict the *ab initio* calculations to such interfaces. The interfaces are assumed to be planar and separate pure phases of Co and WC, i.e., the solubility of W and C in the binder phase is neglected. It is known that Co does not solve in WC [16]. Furthermore, since the WC grains are formed during liquid phase sintering, where the temperature exceeds the Co Curie temperature, Co is taken to be paramagnetic.

The interface energy can be defined as the excess Gibbs free energy due to the presence of the interface. It is related to the free surface energies σ of the corresponding contact surfaces via the Dupré equation; $\gamma_{Co/WC} = \sigma_{Co} + \sigma_{WC} - \sigma_{VC}$ Wsep,Co/WC. Wsep,Co/WC is the ideal work of separation (adhesion energy) of the Co/WC interface, i.e., the reversible work needed to separate the interface into the two free surfaces, neglecting all dissipative processes [3]. In the calculations, the Gibbs free energy is approximated with the internal total energy [17]. This is the dominating contribution to the interface energetics, and the other terms are neglected based on the assumption of them being small together with a tendency for cancellation of temperature dependent terms for differences in free energy between the considered structures [18]. W_{sep,Co/WC} for interfaces constructed from prismatic WC surfaces has been calculated in Ref. [13], together with the Co surface energy. Here we determine the WC surface energy. It can be calculated as $\sigma_{\rm WC} = \frac{1}{A} [E - \mu_{\rm WC} N_{\rm W} - \mu_{\rm C} (N_{\rm W} - N_{\rm C})], \text{ where } E \text{ is the}$ total energy of the surface system with area A, $\mu_{\rm W}(\mu_{\rm C})$ and $N_{\rm W}(N_{\rm C})$ are the W(C) chemical potential and number of W(C) atoms in the system, respectively. The WC bulk chemical potential μ_{WC} is a fixed value calculated from the WC bulk structure. The carbon chemical potential is calculated in the graphite limit [19], and allowed to vary in the interval given by the equilibrium boundaries of the 2phase field {WC + Co binder} in the WC-Co phase diagram [14].

The energy of the prismatic WC $\{10\overline{1}0\}$ surfaces can not be calculated using the standard supercell slab model geometry. This is due to the WC geometry, which lacks any mirror plane with a $\langle 10\overline{1}0 \rangle$ normal. Hence, the two surfaces in the supercell will be nonequivalent. They are denoted type I and II, respectively. For the difference between them, see Fig. 3 and its caption. We have solved this problem by using a triangular model geometry, bounded by only one type of prismatic surface. The calculated excess energy then contains contributions from both the prismatic surfaces and the edges between them. By investigating how the excess energy scales with the boundary length of the triangle, and extrapolating to infinite length, the surface energies of the separate prismatic surfaces can be extracted (see Fig. 2). The validity of the method is verified by comparing the average value of type I and type II carbon terminated surface energies, which is accessible from standard supercell slab calculations and equal to 5.88 J/m², with the present result, 5.92 J/m², obtained with the triangular geometry. The agreement between the two results demonstrates that the computational method using triangular geometries gives accurate values of the surface energies.

The Co/WC($10\overline{10}$) interfaces are modeled using the standard supercell slab geometery. The more ductile metal phase is stretched to obtain coherent interfaces. At the same time, the Co interlayer distances parallel to the interface are relaxed to minimize the introduced strain energy. In computing the interface energy, the strain energy is cancelled out by subtracting the corresponding bulk energy values. In this way the chemical part of the interfacial



FIG. 2. Excess energies, i.e., surface energies plus edge energies, calculated in the graphite limit for three different sizes of triangular geometries with carbon terminated WC{1010} surfaces of type I and II. L denotes the total boundary length of the triangular geometry in units of the lattice constant. The surface energies are given by an extrapolation of the calculated excess energies to $L^{-1} = 0$.



FIG. 3. Part of the atomic configurations within a supercell slab geometry, demonstrating the relative positions of the interface atoms at the type I and type II Co/WC($10\overline{10}$) interfaces. Only tungsten terminated interfaces are displayed. At a type I (II) interface, a carbon atom closest to the interface has four (two) nearest neighbors in the tungsten interface layer, with a carbon-tungsten interplane distance of 0.84 (1.67) Å. Three different translation states for each type of interface are considered, where the interface cobalt atoms occupies top (a), bridge (b), and hollow (c) sites on the tungsten terminated WC surface. For carbon terminated interfaces, W and C atoms are interchanged.

energy is extracted [21]. For each type of interface (I and II) and termination of the carbide grain we have considered three different atomic configurations (see Fig. 3) or translation states on the corresponding γ surface [2].

The most stable Co/WC interfaces are found to be W terminated, and therefore only those are now being considered. The results are summarized in Table I. The stability is to a large degree determined by the atomic coordination of the interface atoms. The stability increases with an increasing number of W nearest neighbors to the interface Co atoms, giving more metal-metal bonding across the interface. Thus, the most stable W terminated Co/WC interfaces for both type I and II are given by translation state (c), independent of carbon chemical potential.

The equilibrium WC shape can be obtained from a Wulff construction [2] as a truncated triangle with $r = (2\gamma_I(\mu_C)/\gamma_{II}(\mu_C) - 1)/(2 - \gamma_I(\mu_C)/\gamma_{II}(\mu_C))$. In the development of the grain shape during liquid phase sintering, there is no structural long-range order in the liquid metal

TABLE I. Co/WC $\{10\overline{1}0\}$ interface energies (in eV/atom) for the structures in Fig. 3.

	η		graphite		
Interface	type I	type II	type I	type II	
(a)	1.30	2.19	1.37	2.34	
(b)	1.06	1.71	1.13	1.86	
(c)	0.35	0.35	0.42	0.50	

phase. The Co atoms can be regarded as mobile, constantly changing the interface structure. It is reasonable to assume that an average value of the interface energy of instantaneous structures given by specific translation states should be representative for the interface energetics. It is however not obvious how different translation states should be weighted in the averaging. We assume that the average can be represented by an integration of the γ surface over an interface unit cell which can be approximated as $\bar{\gamma} =$ $(\gamma_a + 2\gamma_b + \gamma_c)/4A$, with γ_i of the separate translation states given by Table I. The resulting average interface energies $\bar{\gamma}$, and the corresponding r parameters, are given in Table II. The interface energies are notoriously difficult to measure. Only some indirect experimental values are available for the Co/WC interface energy stating that $\gamma_{\rm Co/WC} > \sim 0.5 \ {\rm J/m^2} \ [22].$

The shape factor *r* is found to be about 0.2, in excellent agreement with the experimental results. It is a consequence of the difference in $\bar{\gamma}$ between the type I and type II interfaces. This difference is caused by the contribution from configurations with high interfacial energies, (a) and (b). The energy for the more stable configuration, (c), is very similar for type I and II. Furthermore, the shape factor is slightly higher in the η limit compared to the graphite limit, also in accordance with the experimental findings. This variation of energy with $\mu_{\rm C}$ has a simple geometrical explanation. To grow one complete layer of a type I interface in the [1010] direction requires adding more C atoms compared to a type II interface.

For a more detailed understanding of the differences between type I and II interfaces, and thereby the grain shape, we analyze the electron structure at the Co/WC interfaces. For this purpose, we focus on the main differences between type I and type II at the maximum and minimum points on the γ surface, corresponding to the translation states (a) and (c) in Fig. 3. A good way to probe the modifications of the interface energetics due to the presence of the interface is to look at the change in density of states (DOS) at the interface. The induced total DOS projected on different interface sites at type I and type II Co/WC interfaces are shown in Fig. 4. It can be seen that there are similarities in the interface, the induced states in

TABLE II. Average interface energy $\bar{\gamma}$ (in J/m²) of type I and II Co/WC{1010} interfaces in the eta and graphite limits, together with the corresponding *r* parameter of the truncated triangle shape geometry. For comparison, the experimental result (r_{exp}) is also given.

=		n			graphite	
	type I	-1	type II	type I	Supino	type II
$\bar{\gamma}$	1.80		2.85	1.94		3.14
r		0.19			0.17	
r _{exp}		0.23 ± 0.03			0.14 ± 0.06	



FIG. 4. Site projected induced density of states at type I and II Co/WC interfaces with notation according to Fig. 3. The figure shows the difference in total density of states for the Co, W, and C atoms closest to the interface as compared to corresponding atoms two atomic layers away from the interface. The vertical lines indicate the Fermi level.

the Co interface layers are confined to an energy region from -5 eV up to the Fermi level. There is a strong correlation in the extension and shape of those states with the states induced in the interface tungsten layer, suggestive of a large degree of covalent bonding across the interface. This is most pronounced at the Co/WC I-(a) interface. These bonds are strong and the interface energy of I-(a) is lowered substantially compared to II-(a). The induced W states for the other interfaces are somewhat different from the case of I-(a), but very similar between themselves. They are more dispersed in energy, and at the same time there is a depletion of states on W at about -11 eV. This can probably be attributed to a decrease in C-W interaction. These similarities between I-(c) and the type II interfaces on the one hand, and the deviating behavior at the I-(a) interface on the other hand, give an explanation to why there is a larger difference in interface energy between (a) interfaces than between (c) interfaces, resulting in larger energy variations over the interface at the type II Co/WC interface.

In conclusion, a quantitative analysis of WC grain shape in sintered WC-Co cemented carbides has been performed using ab initio calculations and TEM. To model the prismatic WC surfaces, which lack mirror symmetry, a technique based on triangular model geometries with extrapolation to infinite size has been developed. The irregular Co/WC interfaces are modeled by analyzing the energies of well-defined local geometrical configurations. The measured grain morphology is adequately reproduced by the *ab initio* calculations. The grains are found to be truncated triangles, where the truncation is somewhat larger in the η limit than in the graphite limit. The theoretical analysis is based on metal terminated grains whose interfaces are found to be most stable. The main factor controlling the interface energetics during sintering is found to be the ability of the interfacial atoms to maximize their atomic coordination, with a corresponding increase in metal-metal bonding across the interface. The difference in energy between interfaces formed by the two nonequivalent set of WC prismatic planes is due to the formation of stronger bonds with more covalent character between low coordinated W and Co atoms at type I interfaces compared to at type II interfaces. A different number of C atoms are required to grow type I and II interfaces in the [1010] direction, causing a grain shape dependence on the carbon potential.

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